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ANALYTICAL REFERENCE SERVICE REPORT ON SAMPLE TYPE II

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

July 1957

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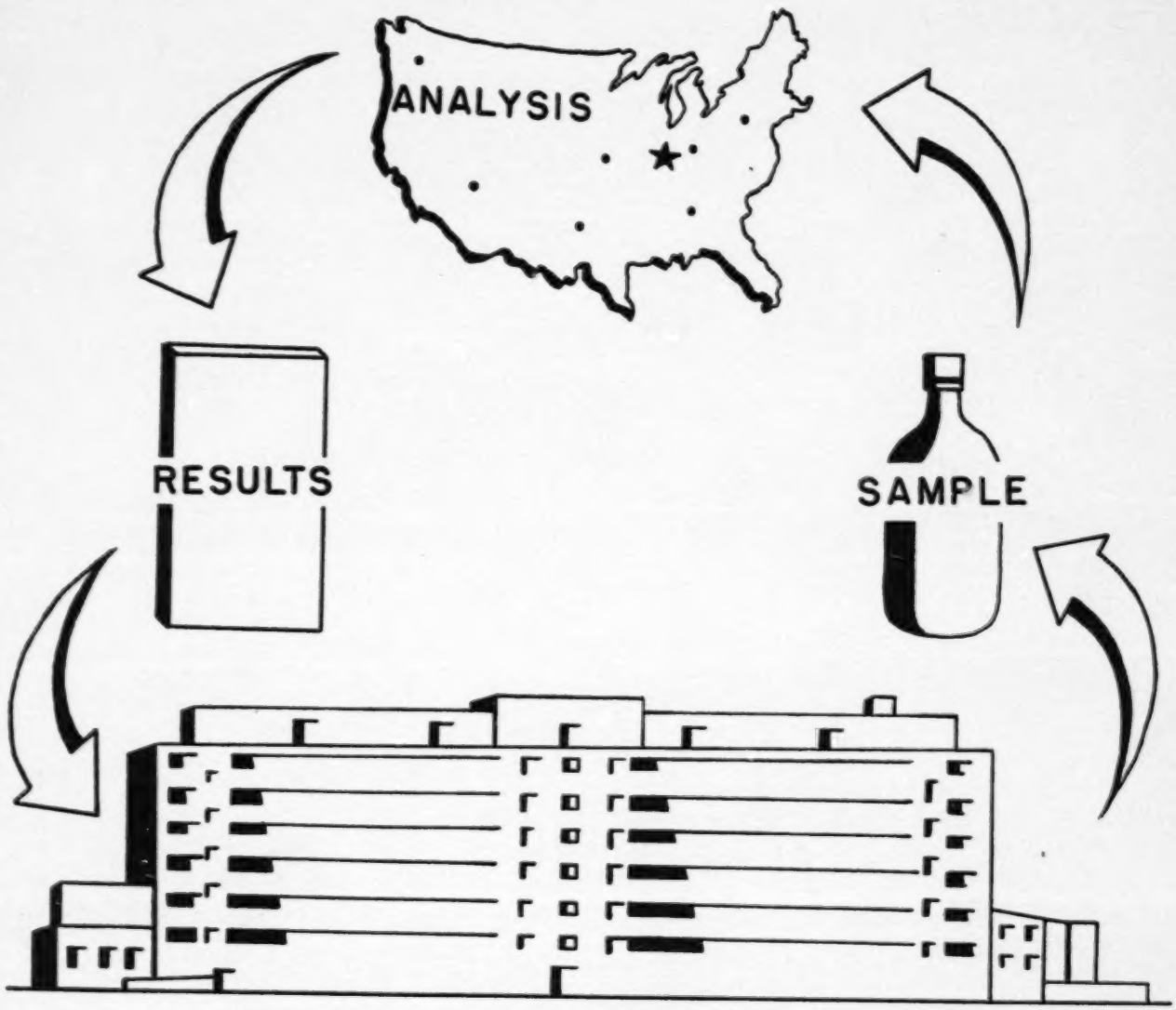

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ANALYTICAL REFERENCE SERVICE

INTRODUCTION

The Analytical Reference Service of the Robert A. Taft Sanitary Engineering Center has as its primary goal the evaluation of laboratory methods in the field of sanitary engineering through the cooperative efforts of organizations having major responsibility for laboratory programs, chiefly state and federal agencies. The exchange of information in addition to the actual experience gained in this type of activity has in the past led to increased proficiency of the participants.

It is believed that through this service a reliable means of evaluation of old and new analytical methods is provided. Other benefits are these:

a. A statistical evaluation of analytical procedures as practiced by similar laboratories using identical samples on a nationwide scale.

b. Exchange of information regarding weaknesses of currently approved methods.

c. An indication to interested research laboratories of methods requiring further development or new approaches.

d. Opportunity for a participating laboratory to evaluate its own procedures and to revise those methods requiring improvement.

PLAN OF OPERATION

Initially, efforts are being directed towards the chemical examination of water. The scope of the program may be broadened gradually to include other types of examinations.

Samples containing measured amounts of the desired constituent are prepared using the most refined grade of chemicals available. Decisions as to the qualitative make up of any particular sample follow suggestions from the member groups and from the Sanitary Engineering Center.

Following preparation of a sample, a notice with a self-addressed reply card is sent to member laboratories announcing the availability and qualitative makeup of the sample. An affirmative reply institutes immediate shipment of a portion of the particular sample, for which a polyethylene container is used. Results are requested within some reasonable period, usually sixty days.

REPORTING OF RESULTS AND COMMENTS

Data are returned to the Sanitary Engineering Center on forms supplied with the sample. Space is provided on the forms for numerical values and a narrative critique of the analytical methods employed.

The values found by the cooperating laboratories are compiled as in the accompanying report. From examination of the combined data, it is hoped that reliable figures relating to accuracy and precision of the methods for the various materials may be obtained. Obviously, the larger the number of laboratories cooperating in a survey, the more reliable the statistical values will be.

It is also strongly desired that all laboratories supply comments on the analytical methods they use. A complete log of pertinent details, difficulties, modifications, sources of error, and other factors would be extremely valuable. Such a compilation of comments could represent an exchange of ideas and opinions that could well become a major part of the final report.

ANALYTICAL REFERENCE SERVICE

MEMBERS AS OF JULY 1, 1957

State Agencies

Arizona State Department of Health
Arkansas State Board of Health
California State Department of Health (Berkeley)
California State Department of Health (Los Angeles)
Colorado State Department of Public Health
Illinois State Water Survey Division
Kentucky State Department of Public Health
Louisiana State Department of Health
Maryland State Department of Health
Maryland Water Pollution Control Commission
Michigan State Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
New Hampshire Water Pollution Commission
New Jersey State Department of Health
New Mexico State Department of Public Health
New York State Conservation Department
New York State Department of Health
North Carolina State Stream Sanitation Committee
Ohio State Department of Health
Oregon State Board of Health
Pennsylvania State Department of Health
South Carolina State Water Pollution Control Authority
South Dakota State Board of Health
Tennessee State Department of Public Health
Texas State Department of Health
Utah State Department of Health
Vermont Department of Health
Vermont Water Conservation Board
Virginia Water Control Board
West Virginia State Water Commission

Federal Agencies

Army Chemical Center, Edgewood, Maryland
Sanitary Engineering Division, 13th Naval District
U. S. Geological Survey, Department of the Interior
Columbus, Ohio
Sacramento, California
Washington, D. C.

Universities

Rutgers University, Department of Sanitation
Purdue University, Department of Chemistry

PARTICIPANTS IN THIS STUDY OF SAMPLE TYPE II

(Distributed October, 1955)

U. S. Geological Survey
Sacramento, California

Utah State Dept. of Health
Ft. Douglas, Utah

W. Va. State Water Comm.
Charleston, West Virginia

Virginia State Water Control Board
Richmond, Virginia

New Jersey State Dept. of Health
Trenton, New Jersey

California Dept. of Health
Berkeley, California

California State Dept. of Health
Los Angeles, California

Arizona State Dept. of Health
Phoenix, Arizona

New York State Dept. of Health
Albany, New York

Department of Public Health & Welfare
Jefferson City, Missouri

Vermont Department of Health
Burlington, Vermont

New Hampshire State Health Department
Concord, New Hampshire

Kentucky State Dept. of Health
Louisville, Kentucky

Tennessee State Dept. of Public Health
Nashville, Tennessee

Montana State Board of Health
Helena, Montana

Oregon State Board of Health
Portland, Oregon

REFERENCE SAMPLE TYPE II

Preparation of Sample

The substrate for Sample Type II consisted of distilled water put through a de-ionizing column. Accurate volumes of standardized solutions of reagent grade chemicals were added to the substrate to furnish the desired concentrations.

The amounts of each metal added to the substrate were as follows:

Aluminum	- 2.00 mg/l	Iron	- 0.55 mg/l
Cadmium	- 0.16 "	Lead	- 0.12 "
Chromium	- 0.15 "	Manganese	- 0.20 "
Copper	- 0.56 "	Zinc	- 7.47 "

Statistical Treatment of Data

Statistical treatment of the data in this report is similar to that used for the Type I minerals sample. * The results obtained at the Sanitary Engineering Center are not included in the calculations since this laboratory was not analyzing an unknown sample. Use of elaborate statistical parameters was not attempted because of the difficulty of interpretation.

The analytical observations returned by the participants are reported most frequently to two decimal places. However, because of differences in the manner of reporting replicate results, all analytical data are listed as received.

Arbitrary rules for treatment of calculated numbers are as follows:

1. The AVERAGE of duplicate or triplicate results are carried to two significant figures.

2. The AVERAGE DEVIATION WITHIN EACH LABORATORY is carried to three significant numbers. This is done because in many cases where a deviation is small (but greater than zero) the first two figures to the right of the decimal are zero,

*Report issued July 2, 1956 on Sample Type I.

i.e., average deviation = .003. For the same reason the AVERAGE DEVIATION FROM THE AMOUNT ADDED is reported to three figures.

3. The PERCENT DEVIATION WITHIN A LABORATORY and the PERCENT DEVIATION FROM THE AMOUNT ADDED are reported to only one decimal place. The practice of reporting a deviation to one hundredth of a percent would be useless where the deviations are so broad.

Significance of the Statistics

The roots of the two parameters, AVERAGE DEVIATION WITHIN EACH LABORATORY AND PERCENT DEVIATION WITHIN EACH LABORATORY, are found in many causes. In theory it should be possible to obtain identical results on aliquots of the same sample. In practice, differences arise from the following:

1. Errors in volumetric techniques, as applied to sample, standards and reagents.
2. Improperly cleaned glassware.
3. Faulty pH control.
4. Dissimilar cuvettes.
5. Unstable photometric equipment.
6. Aging of solutions.
7. Photosensitivity of colored solutions.
8. Other miscellaneous reasons.

In cases where a wide deviation in results within a laboratory appear, a reexamination of techniques may be required. It should be recognized, of course, that certain procedures, because of the complexity of manipulation or other reasons beyond the control of the operator, are incapable of yielding high precision.

The parameters described as AVERAGE DEVIATION FROM AMOUNT ADDED and PERCENT DEVIATION FROM AMOUNT ADDED are a reflection of both the personal competency of the operator and of the efficiency of the analytical procedure used. In some cases, the skill of the analyst may be beyond question, but because of some primary mistake, such as incorrect standards, the final results are in serious

error. However, where the majority of the data show a wide deviation from the amount added it is more reasonable to assume that the source of error is inherent in the method and is not the fault of the analyst. This statement is illustrated by the bar charts which show that almost all laboratories obtain good results on the iron determination, but few obtain acceptable results on aluminum.

Identification of Methods

Under the column headed METHOD, the analytical procedure used by each laboratory is listed. In the large majority of cases, the source of the method used is Standard Methods for the Examination of Water, Sewage and Industrial Wastes, Tenth Edition. However, in some cases, the method is named, but the reference is incomplete with regard to source, edition or page number. In such cases, the information is reported only as supplied. In the preparation of future reports more definite information will be requested from the participants.

A report of this type would be incomplete if some standard of accuracy were not provided for the various analytical procedures used to measure the different metals. In order that the "standard accuracy" of the methods be directly related to the laboratories performing the analysis, the term "50% range" has been used. This figure is defined as the maximum deviation for the best half (50%) of all the results reported for each metal. For example, in the aluminum determination, twelve results were reported with figures ranging from 1.76 mg/l to 5.70 mg/l, of which six were within 0.98 mg/l of the true value. This figure 0.98 is designated as the "50% range" or the range, in milligrams, within which the best half of all results will fall. This arbitrary value may serve as a basis of comparison of results. Any laboratory whose results do not differ from the amount added by more than the 50% range has performed as well, or better, than half of the participants for that particular analysis.

Comments on Sample Type II

All of the procedures for the required analyses appear in both the 9th and 10th editions of Standard Methods for the Examination of Water, Sewage and Industrial Wastes. It was anticipated that all of the participating laboratories would perform some of the analysis routinely and would have special interests in others. However, as state laboratory programs are gradually broadened in efforts to characterize water quality more effectively, all of these analyses will become more significant and more routine.

As previously stated, Sample Type II contained eight different metals ranging from a low concentration of 0.12 mg/l for lead to a high of 7.47 mg/l for zinc. The only interferences present were the various anions added to the sample along with the metals and the

actual metals themselves. Iron interfered in both the aluminum and copper determinations. Zinc presented a hazard in the copper measurement. Chromium could interfere in the manganese determination and every metal was a potential interferer in the dithizone procedures for zinc, cadmium and lead. Lacking specific instructions for removal of certain interferences, some modifications of the usual methods were required.

Accurate measurement of the components of this Type II sample using colorimetric methods posed a difficult analytical problem requiring a high order of professional skill. Two general observations can be drawn from this sample:

1. For six of the eight metals (chromium, copper, iron, lead, manganese and zinc) experience and personal competence are leading factors in obtaining accurate results.

2. The methods currently employed for the measurement of aluminum and cadmium are not satisfactory and require considerable improvement.

ALUMINUM

For the aluminum analysis eleven laboratories reported, with laboratory #9 reporting two results.

The principle method used for this determination is aurin tricarboxylic acid ("Aluminon") reagent, which is the procedure recommended by Standard Methods, 10th edition. The method is deceptively simple since only two reagents are required. However, iron and chromium are said to be positive interferences and no method is given for removal of these interferers. The hematoxylin procedure which is outlined in ASTM Manual on Industrial Water (Tech. Pub. #148-A) requires eight reagents in addition to the Aluminum standards. This procedure provides for removal of iron, but is complex and time consuming.

Whichever method was used, the results in general were poor. Among the 12 measurements reported, one was within 10% and only three were within 25% of the amount added.

On the basis of the figures obtained in this survey, it definitely appears that personal competence is a minor factor in obtaining acceptable analytical results with aluminum. An improved, reliable method is needed.

Summary:

Amount Aluminum Added - 2.0 mg/l

Average Deviation from Amount Added	- 1.404 mg/l
Standard Deviation from Amount Added	- 1.881
50% Range	- 0.98

Method most commonly used	- Aluminon
Method preferred	- Aluminon

These observations are based on twelve reported results.

CADMIUM

Of the eight metals contained in this sample, cadmium is definitely the most difficult metal to measure. Only seven of the participating laboratories performed the analysis and only one laboratory reported a result within 10% of the true value. The comments indicate that most of the laboratories encountered some difficulty. Half reported using modifications of the Standard Methods outline or procedures given elsewhere. On the basis of results completed here, an improved method for cadmium is needed.

Summary:

Amount Cadmium Added - 0.16 mg/l

Average Deviation from Amount Added	- 0.049 mg/l
Standard Deviation from Amount Added	- 0.065
50% Range	- 0.04

Method most commonly used	- dithizone
Method preferred	- no choice

These observations are based on six reported results.
Laboratory #6 not included.

CHROMIUM

For the chromium analysis, 13 laboratories reported with laboratory #9 reporting two different procedures. Only two of the 14 results reported were higher than the amount added. However, 50% of all groups were within 10% of the true amount and nearly 80% were within 20%. Since the amount added was only 0.15 mg/l, 20% deviation represents an error of only 0.03 mg/l.

One fact stands out in this analysis, namely, the metal was added as hexavalent chromium in the form of potassium chromate. However, six groups report absence of hexavalent chromium. Apparently all of the metal reverted to the trivalent state under the acid conditions of the sample.

The consistent loss of chromium in the reported results possibly reflects three different reasons for the low value:

1. Possible loss of chromium by adsorption on the walls of the polyethylene container (This reason cannot be discounted until contrary data are available).
2. Loss of chromium by volatilization during digestion periods.
3. Mechanical loss introduced in transfer and filtering operations.

A fourth source of error in the analysis is the presence of colloidal manganese dioxide in the filtrate after the permanganate has been reduced (St. Meths. - 10th ed., pp. 86). It is suggested that the azide reduction of permanganate which eliminates the filtering operation may be substituted.

Summary:

Amount Chromium Added - 0.15 mg/l

Average Deviation from Amount Added	- 0.026 mg/l
Standard Deviation from Amount Added	- 0.133
50% Range	- 0.01

Method most commonly used - diphenylcarbazide
Method preferred - diphenylcarbazide

Observations based on 14 reported results.

COPPER

For a number of reasons the copper determination is one of the more important measurements made in the heavy metals group. Fourteen of the cooperating groups completed the analysis using two different procedures, namely the "cuprethol" and the "dithiocarbamate" procedures. One laboratory reported perfect results using a dithizone method. Two laboratories did not furnish sufficient information to enable identification of the method used.

Of the total group, only 40% reported values within 10% accuracy. It appears from examination of the data and bar graphs that the error tendency is toward high results. Zinc and iron present in the sample are positive interferers and are the probable cause of error. However, among the five laboratories known to use the "cuprethol" method, the average percent deviation from the amount added was 10.8%, whereas, six laboratories using the dithiocarbamate method had an average deviation of 43.3%. The provision for iron removal in the Standard Methods "cuprethol" procedure apparently accounts for its superiorty.

Summary:

Amount Copper Added - 0.56 mg/l

Average Deviation from Amount Added	- 0.15 mg/l
Standard Deviation from Amount Added	- 0.204
50% Range	- 0.07

Method most commonly used	- diethyldithiocarbamate
Method preferred	- dihydroxyethyldithiocarbamate

Observations based on 14 reported values.

IRON

All of the 16 laboratories cooperating in this survey completed the iron analysis, with laboratory #9 furnishing two figures. The total results are very good, since 14 of the 17 results are within 15% of the true value and 11 (or 65%) of the groups are within 10% of the amount added.

There are essentially two different methods available for the iron measurement, namely the thiocyanate and the o-phenanthroline methods. The o-phenanthroline, bipyridyl and tripyridyl reagents are chemically related and require identical conditions of oxidation state and pH for completion of the color reaction. In addition, the o-phenanthroline procedure can be modified by an extraction operation which employs di-isopropyl ether to remove iron from interferences prior to the o-phenanthroline addition. Both the thiocyanate and phenanthroline produced good results.

Significantly, two laboratories which employed the extraction procedure submitted high results. The possibility of trace amounts of iron in the isopropyl ether cannot be dismissed.

Comparison of the available procedures does not indicate a superior method. However, on the basis of color stability and absence of pH control, the o-phenanthroline, bi- and tripyridyl procedures would seem to be the method of choice.

Summary:

Amount Iron Added - 0.55 mg/l

Average Deviation from Amount Added - 0.087 mg/l
Standard Deviation from Amount Added - 0.126
50% Range - 0.05

Method most commonly used - phenanthroline
Method preferred - phenanthroline

Observations based on 17 reported values.

LEAD

Thirteen laboratories reported figures for lead content of the sample, with laboratory #15 using two procedures, the dithizone and polarograph. Normally, the dithizone procedure is the only available method for lead measurement in low concentrations. Three laboratories (#3, 12, 14) reported perfect or nearly perfect values, while a total of nine laboratories (better than 50%) were within 20% of the amount added. In view of the complexity of the method for removal of interfering materials, personal competence becomes a major factor in performance of this analysis.

Summary:

Amount Lead Added - 0.12 mg/l

Average Deviation from Amount Added	- 0.027 mg/l
Standard Deviation from Amount Added	- 0.311
50% Range	- 0.04

Method most commonly used	- dithizone
Method preferred	- no choice

Observation based on 13 reported values.

MANGANESE

Every laboratory which received a portion of the sample reported values for the manganese determination. Laboratory #9 reported two values for a total of 17 manganese measurements. The results were randomly distributed between high and low measurements with three groups returning perfect or nearly perfect figures.

Two methods, the persulfate and periodate oxidations are the only methods employed for this determination. The persulfate procedure is capable of faster results, but also is more liable to error, since an excess of oxidant must be maintained at all times. Further, the oxidant decomposes at near boiling termperatures and therefore, rapid cooling of the sample is required. In the periodate method the reagent is more stable to heat, so that an excess of reagent is always maintained, once it is added. While both procedures are capable of giving good results, it appears that the periodate method is less subject to error. Eight groups reported using periodate reagent with an average deviation from amount added of 24.6%. Seven groups using the persulfate oxidation had a 52.2% deviation from the amount added.

It is possible that the "special solution" used in the persulfate solution did not tie up the amount of chloride ion present in this sample in which case the results would be in error. (See "Comments" by laboratories #4 and 14).

Summary:

Amount Manganese Added - 0.20 mg/l

Average Deviation from Amount Added	- 0.069 mg/l
Standard Deviation from Amount Added	- 0.100
50% Range	- 0.03

Method most commonly used - periodate
Method preferred - periodate

These observations based on 17 reported results.

ZINC

The zinc content of the sample was 7.47 mg/l. Because of this relatively high concentration, gross errors in the procedure are not reflected in large percentage errors. Out of 11 laboratories reporting values for zinc, 10 were within 25% of the amount added. It is not possible to predict what the "percent deviation from the amount added" would be, had the zinc concentration been in the range of 1.0 mg/l. However, in view of the large dilution factors used in this procedure, the ease of zinc contamination from glassware, and the complexity of separation, the overall accuracy is very good.

Summary:

Amount Zinc Added - 7.47 mg/l

Average Deviation from Amount Added	- 1.33 mg/l
Standard Deviation from Amount Added	- 2.268
50% Range	- 0.60

Method most commonly used - dithizone
Method preferred - no choice

Observations based on 11 reported values.

SUMMARY OF RESULTS

ALUMINUM

Amount Added = 2.0 mg/l

Lab No.	Replicates	Average	Average Deviation Within Each Lab mg/l	Average Deviation Within Each Lab Per cent	Average Deviation from Amount Added mg/l	Average Deviation from Amount Added Per cent	Method
1	5.5 5.9 5.7	5.70	.133	2.3	+3.700	+185.0	Colorimetric Ferron Anal. Chem. 6, pp 710, 1949
2	--- --- ---						
3	2.50 2.50 2.49	2.50	.003	0.1	+0.497	+24.8	Aluminon St. Meth. -10th ed.
4	3.00 3.00 2.60	2.87	.177	6.1	+0.867	+43.3	Aluminon St. Meth. -10th ed. pp 38
5	4.5 4.8 4.6	4.63	.110	2.4	+2.633	+131.7	Aluminon St. Meth. -10th ed. pp 38
6	3.0 3.5 3.5	3.33	.223	6.7	+1.333	+66.7	Aluminon St. Meth. -10th ed. pp 38
7	--- --- ---						
8	--- --- ---						
9A	1.76 --- ---	1.76	---	---	-0.240	-12.0	Aluminon
9B	1.80 1.80 ---	1.80	.000	0.0	-0.200	-10.0	See comments
10	--- --- ---						

11	2.50 2.50 2.57	2.52	.030	1.2	+0.523	+26.2	Hematoxylin Method St. Meth. -9th ed.
12	3.00 3.10 2.84	2.98	.093	3.1	+0.980	+49.0	Aluminon St. Meth.
13	5.0 5.0 5.0	5.00	.000	0.0	+3.000	+150.0	Aluminon St. Meth. -10th ed. pp 38
14	4.0 4.0 4.0	4.00	.000	0.0	+2.000	+100.0	Aluminon St. Meth. -9th ed.
15	--- --- ---						
16	4.00 4.25 4.30	4.18	.123	2.9	+2.183	+109.2	Aluminon St. Meth. -10th ed.
SEC	1.8 1.9 2.0	1.90	.067	3.5	-0.100	-5.0	Hematoxylin Method (ASTM-D 857-50)

COMMENTS ON ALUMINUM

Laboratory 1: No comment made.

Laboratory 2: No comment made.

Laboratory 3: Standard Methods, 10th edition.

Laboratory 4: Method is clear cut and rapid. No difficulties encountered.

Laboratory 5: Aluminon solution must be added to samples individually and optical density must be read at exactly 15 minutes. Temperature must also be kept standard. This makes it rather difficult to obtain comparable results. The interference of phosphates and iron also make the method rather impractical for use on industrial wastes samples.

Laboratory 6: Not included in routine analysis.

Laboratory 7: No comment made.

Laboratory 8: No comment made.

Laboratory 9: Two methods were used in determining aluminum:

Method A - The British Drug House Spot Test using aurine tricarboxylic acid (aluminon). THE BRITISH DRUG HOUSES, Ltd., B.D.H. LABORATORY CHEMICALS GROUP, Poole, England.

A very simple rapid method for determining aluminum. May not be extremely sensitive but appears to be a good method for routine analysis. The determination of aluminum is not ordinarily made in our laboratory.

Method B - Photometric Determination of Aluminum. C. L. Luke and K. C. Braun, ANALYTICAL CHEMISTRY, Vol. 24, Page 1120, July 1952.

A difficult and involved procedure, time-consuming. Experienced difficulty in obtaining and storing the complexing agent, thioglycollic acid. Removal of interferences appears excellent but there is some question as to whether the advantages to be gained by the use of this method in preference to Method A are warranted.

Laboratory 10: No comment made.

Laboratory 11: Standard Methods, 9th edition, hematoxylin procedure, visual comparison.

We prefer this method for visual comparison in our routine work as the color changes are easier to distinguish and the time element is not so critical. We also made an aluminum determination using aluminon reagent, and reading on the Coleman Spectrophotometer which checked very close to the hematoxylin determination.

Our conclusion would be that for water in this state, where aluminum is only occasionally present, the hematoxylin method offers considerable saving of time.

Laboratory 12: No comment made.

Laboratory 13: No difficulty encountered.

Laboratory 14: This was run by the city chemist, who is using the aluminon method from Standard Methods, 9th edition, at both water treatment plants and has used this method for six years. They state that the curve they use is not good above 0.5 ppm and that different batches of aluminon give very different curves.

Laboratory 15: No comment made.

Laboratory 16: Chromium interference.

CADMIUM

Amount Added = 0.16 mg/l

Lab No.	Replicates	Average	Average Deviation Within Each Lab mg/l	Average Deviation Within Each Lab Per cent	Average Deviation from Amount Added mg/l	Average Deviation from Amount Added Per cent	Method
1	--- --- ---						
2	--- --- ---						
3	0.21 0.23 0.22	0.22	.007	3.2	+.060	+37.5	Dithizone St. Meth. -10th ed.
4	0.26 0.28 0.20	0.24	.033	13.5	+.087	+54.4	St. Meth. (modified)
5	0.151 0.152 0.147	0.15	.002	1.3	-.010	-6.7	St. Meth. -10th ed. pp 305-307
6	2.6 2.4 2.3	2.43	.11	4.5	+2.28	+1422.	St. Meth. -10th ed.
7	--- --- ---						
8	--- --- ---						
9	0.128 0.126 ---	0.13	.003	2.3	-.033	-20.6	Dithizone Monocolor meth.
10	--- --- ---						
11	0.12 0.11 0.13	0.12	.007	5.8	-.040	-25.0	St. Meth. -9th ed.

12	--- --- ---						
13	--- --- ---						
14	--- --- ---						
15	0.25 --- ---	0.25	---	---	+.090	+56.2	Polarograph
16	--- --- ---						
SEC	0.18 0.18 0.18	0.18	.000	0 0	+.020	+12.5	St. Meth. -10th ed. (modified)

COMMENTS ON CADMIUM

Laboratory 1: No comment made.

Laboratory 2: No comment made.

Laboratory 3: Standard Methods, 10th edition.

Laboratory 4: Standard Methods, 10th edition, page 305. This procedure was tried in detail on both the check sample and the standard. Very erratic results were obtained. Often no color was obtained even with standards.

The method was modified at sec. 5. 5, page 307 by adding one ml of 20% hydroxylamine hydrochloride aqueous with the 10% sodium hydroxide. However, results with this modification were still erratic.

Finally, the method was modified at sec. 5. 7 by adding one ml of the hydroxylamine solution to the 2% sodium hydroxide. Reasonable extractions were obtained with the standards, but because of the lack of time, no further work was done.

Note: Sandell recommends use of hydroxylamine for strong alkaline dithizone extractions. The method followed exactly as given in the 10th edition did not work even on standards.

The standard procedure gave no recovery of cadmium even from standards. The final carbon tetrachloride - dithizonate extract was yellow-brown. This work was also repeated in subdued light. No recovery of the low cadmium standards in up to micrograms was possible. The 2% sodium hydroxide solution stripped the color out of the carbon tetrachloride solution.

Better results were found when samples and standards were first extracted at pH 9. 5:

1. With amonium hydroxide tartrate and hydroxylamine and chloroform - dithizone.
2. Chloroform - dithizone extract washed with normal hydrochloric acid.
3. Chloroform - dithizone discarded.
4. pH of acid solution to 8. 5 with ammonium hydroxide.
5. Extract with chloroform - dithizone.
6. Extracts washed with 2% sodium hydroxide.

Results good for standards but more work on same line needed to eliminate interferences.

Laboratory 5: Difficult to tell when all of the cadmium has been extracted by the dithizone. After all of the cadmium had been extracted, the zinc dithizonate continued to give a red color. This, however, does not interfere with the method as the zinc dithizonate is removed by the final washing with 2 percent sodium hydroxide solution.

Method is a considerable improvement over the method previously used in time spent.

General comments:

It would be much more convenient if all of the dithizone methods could be prepared from a single stock solution.

In preparing the sample, the digestion used in this laboratory consists of bringing the sample to fumes with 5 ml. concentrated sulfuric acid and then adding concentrated nitric acid dropwise until the liquid is colorless. This method takes much less time than the procedure in the 10th edition of Standard Methods (p. 304), with no apparent loss of metals.

Laboratory 6:	Cadmium nitrate used as a standard. No carbon tetrachloride was available, therefore all extractions and reagents made with chloroform. Not done routinely.
Laboratory 7:	No comment made.
Laboratory 8:	No comment made.
Laboratory 9:	Colorimetric Micro-Determination of Chromium with Dithizone, Bernard E. Saltzman, ANALYTICAL CHEMISTRY, Vol. 25, page 493, March 1953. An excellent, straightforward, direct method. Colors are very stable and much greater tolerance to interfering metals is allowed. Improved separation of interfering substances is achieved by the use of small amounts of cyanide as a suppressing agent, tartaric acid as a stripping medium. We do not determine this element routinely in our laboratory.
Laboratory 10:	No comment made.
Laboratory 11:	Using the Standard Methods, 10th edition procedure, we were unable to obtain as good checks as we would like for the determination. For that reason we used a procedure developed by Goldman as the U. S. P. H. for the Industrial Hygiene Service. This is a dithizone extraction procedure and gave us very close agreement on our three determinations.
Laboratory 12:	Not done in our lab.
Laboratory 13:	No modification of dithizone method was successful. The large amount of zinc contained in sample made it necessary for inumerable extractions, in which small amounts of cadmium could be lost. Addition of reducing agents did not make any significant differences in the difficulties encountered.
Laboratory 14:	Not set up for cadmium determinations.
Laboratory 15:	No comment made.
Laboratory 16:	No comment made.

CHROMIUM

Amount Added = 0.15 mg/l

Lab No.	Replicates	Average	Average Deviation Within Each Lab mg/l	Average Deviation Within Each Lab Per cent	Average Deviation from Amount Added mg/l	Average Deviation from Amount Added Per cent	Method
1	0.05 0.05 0.06	0.05	.003	6.0	-.097	-64.5	Diphenylcarbazide (Colorimetric Determination of traces of metals 2 Ed., 1950)
2	0.08 0.08 0.08	0.08	.000	0.0	-.070	-46.7	Diphenylcarbazide St. Meth.
3	0.143 0.152 0.146	0.15	.003	2.0	-.003	- 2.0	Permanganate oxidation St. Meth.-10th ed.
4	0.15 0.15 0.15	0.15	.000	0.0	.000	0.0	Bromate Procedure St. Meth.
5	0.12 0.12 0.12	0.12	.000	0.0	-.030	-20.0	Diphenylcarbazide St. Meth.-10th ed. pp 308-309
6	0.16 0.16 0.15	0.16	.003	1.9	+.007	+ 4.5	Alkaline bromate oxidation St. Meth.-10th ed.
7	--- --- ---						
8	--- --- ---						
9A	0.13 --- ---	0.13	---	---	-.020	-13.3	Diphenylcarbazide See comments
9B	0.16 --- ---	0.16	---	---	+.010	+ 6.7	Diphenylcarbazide See comments
10	0.118 0.118 0.122	0.12	.002	1.7	-.031	-20.5	Alkaline bromate oxidation St. Meth.-10th ed. pp 85

11	0.13 0.13 0.13	0.13	.000	0.0	-.020	-13.3	Diphenylcarbazide St. Meth.-10th ed.
12	0.140 0.146 0.156	0.15	.006	4.1	-.003	- 1.8	Diphenylcarbazide St. Meth.
13	0.075 0.100 0.075	0.08	.011	13.2	-.067	-44.5	Diphenylcarbazide St. Meth.-10th ed. pp 84
14	0.152 0.140 0.140	0.14	.005	3.5	-.006	- 4.0	Hexavalent & Total St. Meth.
15	0.12 0.15 0.16	0.14	.017	12.1	-.007	- 4.5	Alkaline bromate oxidation
16	--- --- ---						
SEC	0.11 0.13 0.13	0.12	.01	8.3	-.027	-17.8	Permanganate method St. Meth.-10th ed. pp 85

COMMENTS ON CHROMIUM

Laboratory 1: Total chromium determined. Hexavalent chromium is zero.

Laboratory 2: Standard Methods.

Laboratory 3: Standard Methods, 10th edition.

Laboratory 4: No hexavalent chromium.

Laboratory 5: The addition of 5 ml. of 5 percent cupferon appeared to give too great an excess unless sample contained an extremely large amount of interfering metals. When this amount was added, the resulting solution was very difficult to oxidize, was time-consuming, and the resulting solution had a yellow color. Between 2-5 ml. of a 1 percent solution of cupferon gave favorable results.

Addition of diphenylcarbazide had to be done individually to each sample. Full color development was reached after 5 minutes and color began to fade immediately thereafter. Color is not stable for 2 hours as stated in the method.

Laboratory 6: Not included in routine analysis.

Laboratory 7: No comments made.

Laboratory 8: No comments made.

Laboratory 9: Two methods were employed in performing this determination:

Method A - Microdetermination of chromium with diphenylcarbazide by permanganate oxidation. Bernard E. Saltzman, paper presented April 23, 1952, at Annual Meeting of AIHA, Cincinnati, Ohio.

This determination not made routinely in our laboratory. A good direct method. Colors clear and stable; interferences rendered negligible.

Method B - Determination of total chromium by the use of permanganate in sulfuric acid with diphenylcarbazide as a color-producing agent. Ruchhoft, Moore, Terhoeven, Middleton and Krieger, TENTATIVE ANALYTICAL METHODS FOR CADIUM, CHROMIUM AND CYANIDE IN WATER, 1949, Environmental Health Center, Cinn., Ohio; also, Standard Methods, 10th edition, 1955.

Same as method A but possibly a little more time-consuming. Note: No hexavalent chromium in this sample.

Laboratory 10:	**No comments made.**
Laboratory 11:	**Standard Methods, 10th edition, total chromium. The sample at the time of analyses did not show hexavalent chromium, so we used the alkaline bromate oxidation which gave very good color reaction. Visual comparison.**
Laboratory 12:	**No comments made.**
Laboratory 13:	**No hexavalent chromium. Sample was brominated. No difficulty was encountered.**
Laboratory 14:	**None detected as hexavalent. Sodium bromate oxidation used. Seems to be satisfactory.**
Laboratory 15:	**No comments made.**
Laboratory 16:	**No comments made.**

COPPER

Amount Added = 0.56 mg/l

Lab No.	Replicates	Average	Average Deviation Within Each Lab mg/l	Average Deviation Within Each Lab Per cent	Average Deviation from Amount Added mg/l	Average Deviation from Amount Added Per cent	Method
1	0.58 0.58 0.59	0.58	.003	0.5	+.023	+ 4.2	Colorimetric Carbamate Dihydroxyethyldithiocarbamic acid
2	0.8 0.8 0.8	0.80	.000	0.0	+.240	+42.9	Carbamate St. Meth.
3	0.48 0.50 0.52	0.50	.013	2.6	-.060	-10.7	Diethyldithiocarbamate St. Meth. - 10th ed.
4	0.58 0.58 0.58	0.58	.000	0.0	+.020	+ 3.6	Method A - "cuprethol" St. Meth. - 10th ed.
5	0.64 0.61 0.57	0.61	.023	3.8	+.047	+ 8.3	Copper with Bis (2 hydroxy ethyl) dithiocarbamate. Butts, Cahler & Mellon (1)
6	0.88 0.81 0.80	0.83	.033	4.0	+.270	+48.2	Diethyldithiocarbamate St. Meth. - 10th ed.
7	--- --- ---						
8	0.40 0.40 0.37	0.39	.013	3.3	-.170	-30.4	Diethyldithiocarbamate St. Meth. - 10th ed. pp 95-96-97
9	0.56 --- ---	0.56	---	.04	.000	0.0	Dithizone (mixed color method) (See comments)
10	0.78 0.87 0.81	0.82	.033	4.0	+.260	+46.4	Diethyldithiocarbamate
11	0.48 0.50 0.48	0.49	.010	2.0	-.073	-13.1	Carbamate St. Meth. - 10th ed.

12	0.795 0.720 0.690	0.735	.043	5.9	+.175	+31.2	"Cuprethol" St. Meth.
13	0.10 0.08 0.08	0.09	.010	11.1	-.473	-84.5	Diethyldithiocarbamate St. Meth. - 10th ed. pp 95
14	0.60 0.60 0.60	0.60	.000	0.0	+.040	+ 7.1	"Cuprethol" St. Meth. - 10th ed.
15	0.84 0.75 0.76	0.78	.037	4.7	+.223	+39.9	Diethyldithiocarbamate
16	--- --- ---						
SEC	0.63 0.63 0.63	0.63	.000	0.0	+.070	+12.5	Diethyldithiocarbamate St. Meth. - 10th ed. pp 95

COMMENTS ON COPPER

Laboratory 1: Colored copper complex exists in true solution and the color is stable.

Laboratory 2: Standard Methods.

Laboratory 3: Standard Methods, 10th edition.

Laboratory 4: Method is clear cut and short.
Alternate procedure, 10th edition, Method B, Diethyldithiocarbamate.
Results: 0.76 0.72 0.74 Average 0.74 mg/liter
Comments: This method gave higher results than the "cuprethol" method. Both methods seem clear cut and do not indicate any visible difficulties in the procedure. We do not know the reason for the higher results by the carbamate method.

Laboratory 5: Reasonably rapid. Good color development. No difficulties were encountered. Method from Standard Method, 10th edition, seemed to give poor separation copper from interfering metals.

Laboratory 6: Reagents not available for "cuprethol" method. Color extracted with carbon tetrachloride.

Laboratory 7: No comments made.

Laboratory 8: No comments made.

Laboratory 9: Simple direct method. Ferric iron interferes.
Dithizone method (mixed color method)
CHEMICAL METHODS IN INDUSTRIAL HYGIENE, F.H. Goldman and M.B. Jacobs; Interscience Publishers, 1953.
This determination not performed routinely in our laboratory. The method is rapid and very direct but it appears that high results are obtained because of the interference of ferric iron.

Laboratory 10: Do not have reagents for "cuprethol" method.

Laboratory 11: Standard Methods, 10th edition, carbamate used. Visual comparison against a series of standards.

Laboratory 12: Replicates: 0.795 0.720 0.690 Average 0.735 mg/liter
Method: Standard Methods "cuprethol" (photometric)
Comments: With our available equipment, namely a Fisher electrophotometer with 425 filter, the method did not appear to be as sensitive as the carbamate method. However, the severe turbidity produced by the carbamate rendered this method useless. No attempt was made to extract the color from carbamate.

Laboratory 13: The color was extracted with carbon tetrachloride. The method seemed to work satisfactorily and was easily performed.

Laboratory 14: Very good.

Laboratory 15: Did not complex (or complete) the iron in 0.84 reading.

Laboratory 16: No comments made.

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IRON

Amount Added = 0.55 mg/l

Lab No.	Replicates	Average	Average Deviation Within Each Lab mg/l	Average Deviation Within Each Lab Per cent	Average Deviation from Amount Added mg/l	Average Deviation from Amount Added Per cent	Method
1	0.58 0.59 0.59	0.59	.003	.51	+.037	+6.7	Colorimetric 2, 2 bipyridine
2	0.5 0.5 0.5	0.50	.000	0.0	.050	-9.1	Thiocynate method St. Meth.
3	0.50 0.50 0.50	0.50	.000	0.0	-.050	-9.1	Tripyridyl St. Meth. -10th ed.
4	0.60 0.60 0.60	0.60	.000	0.0	+.050	+9.1	Bipyridyl St. Meth.
5	0.72 0.74 0.71	0.72	.010	1.4	+.173	+31.5	Phenanthroline St. Meth. -10th ed. pp 312-313
6	0.62 0.62 0.60	0.61	.010	1.6	+.063	+11.5	Bipyridine St. Meth. -9th ed.
7	0.5 0.5 0.5	0.50	.000	0.0	-.050	-9.1	Taylor Slide Comparator
8	0.24 0.24 0.24	0.24	.000	0.0	-.310	-56.4	Phenanthroline St. Meth. -10th ed. pp 125-26 27-28
9A	0.85 0.85 ---	0.85	.000	0.0	+.300	+54.5	Phenanthroline St. Meth.
9B	0.60 0.56 ---	0.58	.013	2.2	+.030	+5.5	Phenanthroline St. Meth.
10	0.6 0.6 0.6	0.60	.000	0.0	+.050	+9.1	Phenanthroline

11	0.6 0.6 0.65	0.62	.023	3.7	+.067	+12.2	Thiocynate method St. Meth. -9th ed.
12	0.52 0.46 0.52	0.50	.027	5.4	-.050	-9.1	Phenanthroline St. Meth.
13	0.50 0.50 0.50	0.50	.000	0.0	-.050	-9.1	Thiocynate
14	0.46 0.48 0.48	0.47	.010	2.1	-.077	-14.0	Bipyridine. St. Meth. -9th ed. Tripyridine. St. Meth. -10th ed.
15	0.507 0.503 0.513	0.51	.004	0.8	-.042	-7.6	Phenanthroline
16	0.51 0.51 0.50	0.51	.003	0.6	-.043	-7.8	Phenanthroline St. Meth. -10th ed.
SEC	0.56 0.53 ---	0.54	.015	2.8	-.005	-0.9	Phenanthroline St. Meth. -10th ed. pp 125

COMMENTS ON IRON

Laboratory 1: No comments made.

Laboratory 2: Standard Methods.

Laboratory 3: Standard Methods, 10th ed.

Laboratory 4: No difficulties encountered in the method.

Laboratory 5: Method is quite simple and appears to give good results. No difficulties were encountered.

Laboratory 6: No comments made.

Laboratory 7: Reagents used: HCl, $KMnO_4$, KSCN.

Laboratory 8: No comments made.

Laboratory 9: Two methods were employed in performing this determination:

Method A - Standard Methods, phenanthroline method employing extraction with diisopropyl ether from 7-8 molar hydrochloric acid.

This method is time-consuming and requires the use of small amounts of sample. Advantages gained by the use of this method are questionable.

Method B - Standard Methods, phenanthroline method, no extraction with ether. A simple, direct, rapid method. Appears excellent for routine analysis.

The determination of iron is made routinely in our laboratory.

Laboratory 10: No comments made.

Laboratory 11: We used the ammonium thiocyanate method for iron for two reasons. First, this is the method we use routinely, and secondly, we did not have reagents for the Standard Methods procedure. Visual comparison.

Laboratory 12: Method reported used 5.0 cm light path. Using 2.0 cm light path, results were: 0.56 0.52 0.58, Av. 0.55.

Laboratory 13: No difficulty encountered. Thiocyanate method was found to be as reliable as bipyridyl or orthophenanthroline methods.

Laboratory 14: Modified so that residue in total solid dish was used. Standard Methods followed per se. Do not have confidence in methods for low iron concentrations of less than 0.2 ppm.

Laboratory 15: No comments made.

Laboratory 16: No comments made.

LEAD

Amount Added = 0.12 mg/l

Lab No.	Replicates	Average	Average Deviation Within Each Lab mg/l	Average Deviation Within Each Lab Per cent	Average Deviation from Amount Added mg/l	Average Deviation from Amount Added Per cent	Method
1	0.13 0.12 0.15	0.13	.010	7.7	+ .013	+11.1	Colorimetric Dithizone Extraction
2	0.08 0.062 ---	0.07	.006	8.6	- .049	-40.8	Dithizone St. Meth.
3	0.12 0.12 0.12	0.12	.000	0.0	.000	0.0	Dithizone St. Meth. - 10th ed.
4	0.12 0.14 0.12	0.13	.010	7.7	+ .007	+ 5.5	Monocolor method St. Meth. - 10th ed. pp 313
5	0.097 0.093 0.095	0.10	.001	1.1	- .025	-20.8	St. Method. - 10th ed. pp 313-317
6	0.22 0.21 0.18	0.20	.017	8.5	+ .083	+69.4	Dithizone mixed color St. Meth. - 10th ed.
7	--- --- ---						
8	0.108 0.108 0.086	0.10	.010	9.9	- .019	-16.1	Dithizone St. Meth. - 10th ed. pp 131-132
9	0.106 --- ---	0.11	---	---	- .014	-11.7	Dithizone. See comments.
10	--- --- ---						
11	0.109 0.111 0.108	0.11	.001	0.9	- .011	- 8.9	Dithizone

12	0.11 0.12 0.14	0.12	.010	8.3	+ .003	+ 2.8	Dithizone mixed color St. Meth.
13	0.190 0.215 0.187	0.20	.012	6.1	+ .077	+64.4	Dithizone extraction St. Meth. & Sandell
14	0.120 0.125 0.125	0.12	.002	1.6	+ .003	+ 2.8	Dithizone St. Meth.
15A	1.36 1.30 1.32	1.33	.023	1.7	+1.207	+1006.0	Dithizone
15B	0.175 --- ---	0.18	---	---	+ .055	+45.8	Polarograph
16	--- --- ---						
SEC	0.14 0.15 0.16	0.15	.007	4.7	+ .030	+25.0	Dithizone (SEC modified) St. Meth. - 10th ed.

COMMENTS ON LEAD

Laboratory 1: No comments made.

Laboratory 2: Standard Methods.

Laboratory 3: Standard Methods, 10th edition.

Laboratory 4: Amounts of reagents excessive (ppt. of salts required considerable amount of water to bring back into solution). Also, a mixed color method would be as applicable after removal of the interfering ions. Danger of loss of the dithizonate salt in washing out the excess dithizone in the procedure may give low results.

Laboratory 5: Method stated for purifying carbon tetrachloride will not work as carbon tetrachloride and alcoholic potassium hydroxide are miscible. Method as described under Cadmium, p. 306, of Standard Methods was used.

When purifying dithizone by the method described, difficulty was encountered in redissolving the dithizone. Better results were obtained when the chloroform or carbon tetrachloride was added before the dithizone was precipitated from the water layer.

Dithizone solutions seemed to be too concentrated for ordinary work.

Method was rather long and tedious.

Laboratory 6: No comments made.

Laboratory 7: No comments made.

Laboratory 8: No comments made.

Laboratory 9: METHODS FOR DETERMINING LEAD IN AIR AND BIOLOGICAL MATERIALS (Dithizone). American Public Health Association, 1955.

An excellent method. Appears to have many advantages for its use as a standard method in routine analysis. This determination is not performed routinely in our laboratory.

Laboratory 10:	No comments made.
Laboratory 11:	We used the mixed color dithizone method, modifying the reagent strength so as to be applicable to the cell width used in the Coleman instrument.
Laboratory 12:	No comments made.
Laboratory 13:	Lead extraction very difficult due to excessive amounts of reagents required to clear interfering ions. Sample had to be wet ashed with hydrogen peroxide. Lead was lost on first several attempts. Mixed color method preferred.
Laboratory 14:	I found it necessary to add the ammoniacal cyanide to the sample during the original dithizone extraction, assuming the copper present was preventing the completion of the extraction. This seems to be a critical point as the volume of extract obtained before complexing the copper was prohibitive. Perhaps a stronger dithizone would also have been the answer.
	Exacting and time-consuming. Necessary to complex the copper before completing the extractions.
Laboratory 15:	No comments made.
Laboratory 16:	No comments made.

MANGANESE

Amount Added = 0.20 mg/l

Lab No.	Replicates	Average	Average Deviation Within Each Lab mg/l	Average Deviation Within Each Lab Per cent	Average Deviation from Amount Added mg/l	Average Deviation from Amount Added Per cent	Method
1	0.20 0.24 0.23	0.22	.017	7.7	+.023	+ 11.7	Periodate
2	0.35 0.35 0.35	0.35	.000	0.0	+.150	+ 75.0	Persulfate St. Meth.
3	0.10 0.10 0.10	0.10	.000	0.0	-.101	- 50.4	Periodate St. Meth.-10th ed.
4	0.24 0.24 0.26	0.25	.010	4.0	+.047	+ 23.4	Persulfate Method B St. Meth.-10th ed.
5	0.12 0.13 0.14	0.13	.007	5.4	-.070	- 35.0	Periodate St. Meth.-10th ed. pp 317-318
6	0.45 0.42 0.42	0.43	.013	3.0	+.230	+115.0	Persulfate St. Meth.-9th ed.
7	0.30 0.20 0.20	0.23	.043	18.7	+.033	+ 16.6	Taylor Slide Comparator
8	0.22 0.21 0.17	0.20	.020	10.0	.000	0.0	Periodate St. Meth.-10th ed. pp 138-139
9A	0.22 --- ---	0.22	---	---	+.020	+ 10.0	Periodate St. Meth.-10th ed.
9B	0.18 0.18 0.18	0.18	.000	0.0	-.020	- 10.0	Persulfate St. Meth.-10th ed.
10	0.17 0.14 0.14	0.15	.013	8.7	-.050	- 25.0	Periodate with pretreatment

11	0.16 0.17 0.16	0.16	.003	1.9	-.037	- 18.4	Persulfate St. Meth.-9th ed.
12	0.215 0.190 ---	0.20	.010	5.0	.000	0.0	Periodate St. Meth.
13	0.0 0.0 0.0	0.00	---	---	-.200	-100.0	Persulfate St. Meth.-10th ed. pp 140
14	0.202 0.210 0.190	0.20	.075	3.7	.000	0.0	Persulfate - Periodate St. Meth.
15	0.08 0.09 0.05	0.07	.017	24.3	-.127	- 63.4	Periodate
16	0.28 0.28 0.27	0.28	.003	1.1	+.077	+ 38.4	Persulfate St. Meth.-10th ed.
SEC	0.20 0.20 0.21	0.20	.003	1.5	+.003	+ 1.6	Periodate St. Meth.-10th ed.

COMMENTS ON MANGANESE

Laboratory 1: No comments made.

Laboratory 2: Standard Methods.

Laboratory 3: Standard Methods, 10th ed.

Laboratory 4: Oxidation using the Standard Methods persulfate procedure and using 5 ml of "special solution" did not work. Insufficient mercuric sulfate to tie up all the chlorides present. Chlorides were determined and the procedure was repeated using 12 ml of "special solution".

Laboratory 5: Method was quite simple and rapid. Color development was good. No apparent difficulty was encountered.

Laboratory 6: Not included in routine analysis.

Laboratory 7: Reagents used: silver nitrate, nitric acid, ammonium persulfate.

Laboratory 8: The addition of silver nitrate seems to give a turbidity. These results were obtained without the addition of silver nitrate.

Laboratory 9: Two methods were employed in making this determination:

Method A - Standard Methods, 10th edition - Periodate Method.

We occasionally determine manganese in our laboratory, employing this method. We find the method simple but slightly time-consuming. We sometimes encounter difficulties with respect to turbidity in the final color development. Chloride ion appears to interfere.

Method B - Standard Methods, 10th edition - Persulfate Method.

A rapid method, apparently less subject to interference from chloride ion, but occasionally rendered unsatisfactory by the unexplained appearance of a precipitate of a mercury salt.

Laboratory 10:	**No comments made.**
Laboratory 11:	**Standard Methods, 9th edition, persulfate oxidation. We were unable to obtain consistent color development with the procedure in the Standard Methods, 10th edition.**
Laboratory 12:	**One sample decolorized almost completely during heating in water bath. Dirty flask? Result not included in average.**
Laboratory 13:	**The analysis was performed by using 5 ml. of "special solution", also by the complete precipitation of chlorides with silver nitrate. The results were the same in each case.**
Laboratory 14:	**Chloride in sample (1180 ppm) seriously interferes and was complexed with excess mercuric sulfate in persulfate method.**
Laboratory 15:	**No comments made.**
Laboratory 16:	**No comments made.**

ZINC

Amount Added = 7.47 mg/l

Lab No.	Replicates	Average	Average Deviation Within Each Lab mg/l	Average Deviation Within Each Lab Per cent	Average Deviation from Amount Added mg/l	Average Deviation from Amount Added Per cent	Method
1	8.8 9.1 9.4	9.10	.200	2.2	+1.63	+21.8	Dithizone Extraction
2	--- --- ---						
3	5.50 5.60 5.60	5.57	.043	0.8	-1.90	-25.5	Dithizone St. Meth. - 10th ed.
4	8.00 8.00 8.00	8.00	.000	0.0	+0.53	+ 7.1	Mixed color dithizone St. Meth. - 10th ed.
5	8.3 8.0 8.1	8.13	.110	1.4	+0.66	+ 8.9	St. Meth. - 10th ed. pp 320-322
6	7.5 7.5 ---	7.50	.000	0.0	+0.03	+ 0.4	Monocolor method St. Meth. - 10th ed.
7	--- --- ---						
8	--- --- ---						
9	8.4 --- ---	8.40	---	---	+0.93	+12.4	Dithizone mixed color method See comments.
10	6.6 6.3 6.8	6.57	.177	2.7	-0.90	-12.1	Volumetric dithizone method
11	8.0 8.0 7.7	7.90	.133	1.7	+0.43	+ 5.8	St. Meth. - 10th ed.

12	9.2 9.6 5.8	8.20	1.600	19.5	+0.73	+ 9.8	Dithizone mixed color St. Meth.
13	7.96 8.23 7.56	7.92	.237	3.0	+0.45	+ 6.0	Dithizone St. Meth. - 10th ed. pp 212
14	--- --- ---						
15	1.02 --- ---	1.02	---	---	-6.45	-86.3	Dithizone
16	--- --- ---						
SEC	7.75 7.90 6.60	7.42	.543	7.3	-0.05	- 0.7	Dithizone St. Meth. - 10th ed. pp 320

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COMMENTS ON ZINC

Laboratory 1: No comments made.

Laboratory 2: No comments made.

Laboratory 3: Standard Methods, 10th edition.

Laboratory 4: No difficulties encountered. Method rapid and precise.

Laboratory 5: After the extraction of methyl red with carbon tetrachloride an extra washing with carbon tetrachloride would insure the removal of the small amount of carbon tetrachloride which remains suspended over the water layer. The methyl red in this small amount of carbon tetrachloride might be enough to interfere with the color development.

The elimination of a preliminary separation of copper and other interfering ions removes the possibility of obtaining low results due to the loss of zinc in the separation step.

Method is reasonably fast and with a minimum amount of manipulation.

Laboratory 6: Used Brom Cresol Green D in solution rather than Brom Cresol Green. Final dilution with chloroform because no more carbon tetrachloride available. Not done routinely.

Laboratory 7: No comments made.

Laboratory 8: No comments made.

Laboratory 9: One method employed which combined the essential features of two recognized procedures.

Standard Methods, 10th edition, mixed color method (dithizone); and E. B. Sandell, COLORIMETRIC DETERMINATION OF TRACE METALS, Mixed color method (dithizone).

Method appears to be too sensitive for the determination of fairly large amounts of zinc, thus necessitating the use of very small quantities of sample and the employment of large arithmetical factors. The method apparently yields high results by interferences which are not removed by the procedure. We do not determine zinc routinely in our laboratory.

Laboratory 10: Found preferable in the presence of iron.

Laboratory 11: Standard Methods, 10th edition procedure. No further comment necessary.

Laboratory 12: Also tried monocolor method. Very erratic results. Procedure much too elaborate for routine use.

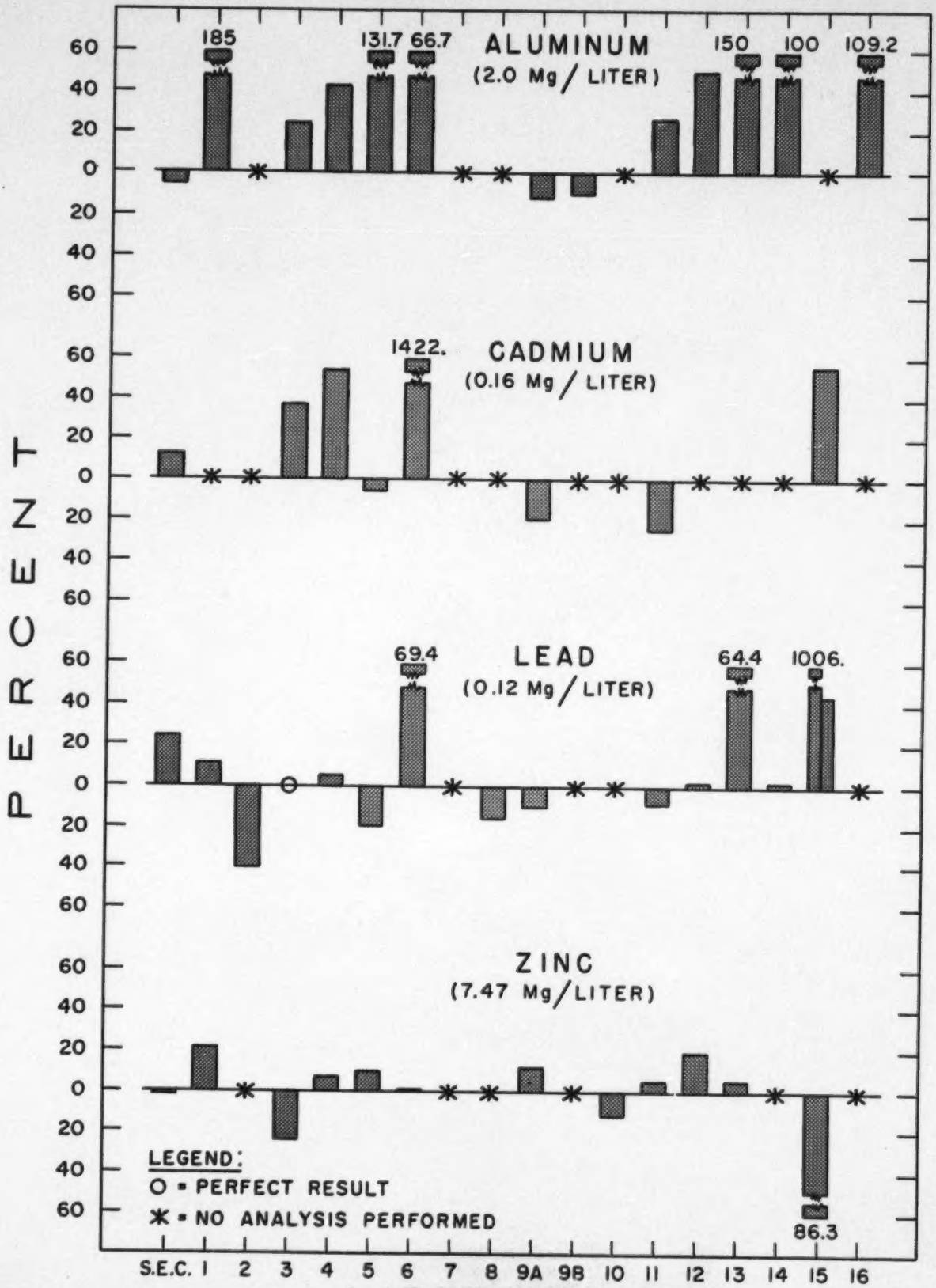
Laboratory 13: No difficulty encountered, probably due to relatively large quantity of zinc.

Laboratory 14: Not set up for zinc determinations.

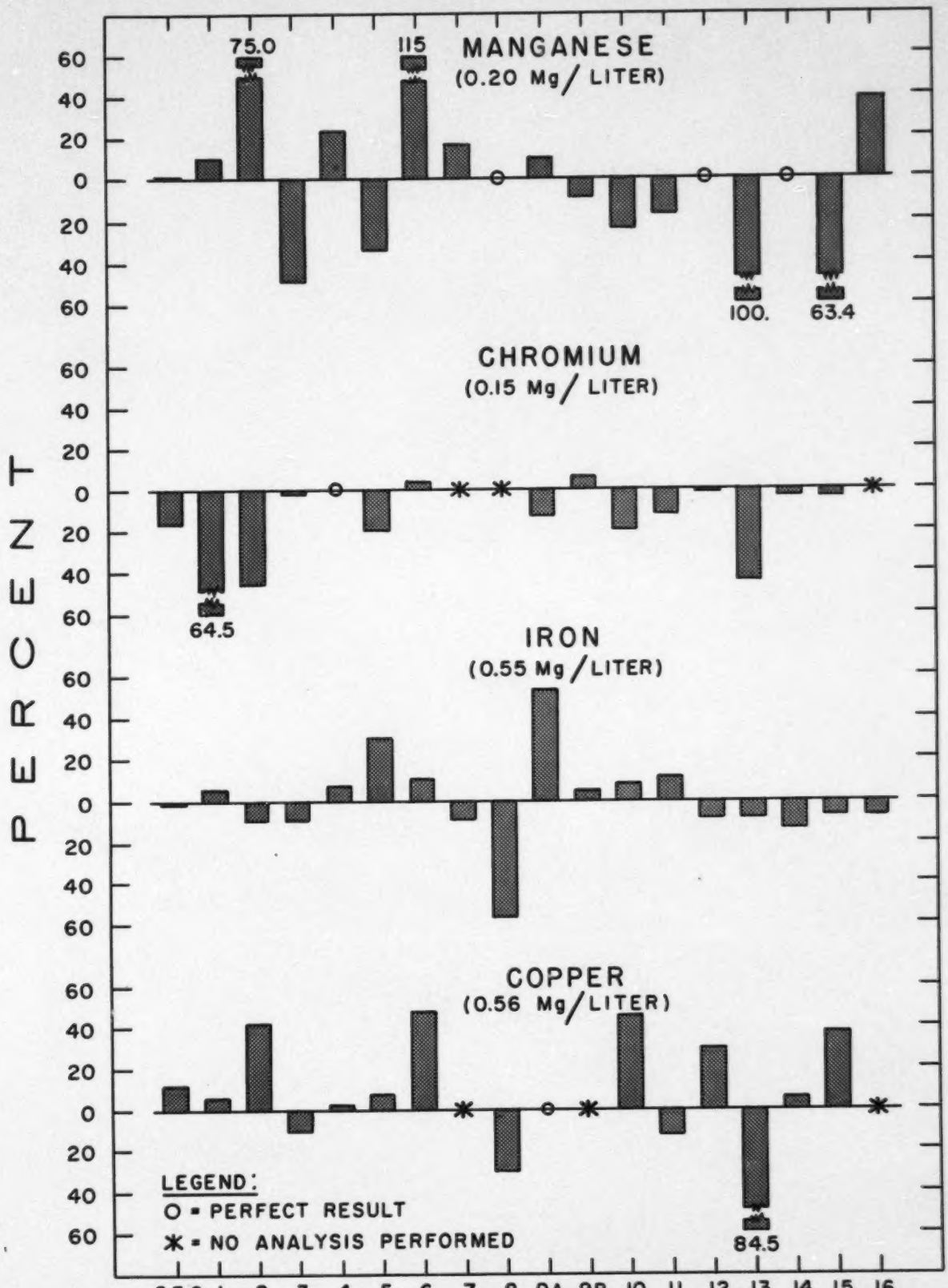
Laboratory 15: No comments made.

Laboratory 16: No comments made.

Determination	Number Of Labs. Reporting	Amount Added mg/l	Arithmetic Mean mg/l	Median Value mg/l	Standard Deviation mg/l	Average Per Cent Deviation	
						Within a Lab.	From Amount Added
Aluminum	11	2.00	3.44	3.16	1.881	2.3	70.2
Cadmium	7	0.16	0.51	0.22	0.065	4.4	30.6
Lead	13	0.12	0.22	0.12	0.311	5.2	22.5
Zinc	11	7.47	7.12	7.92	2.268	3.5	17.8
Chromium	13	0.15	0.13	0.14	0.133	3.7	17.3
Manganese	15	0.20	0.20	0.20	0.100	6.2	34.5
Copper	14	0.56	0.60	0.59	0.204	3.2	26.4
Iron	16	0.55	0.55	0.51	0.126	1.1	15.8



PERCENT DEVIATION FROM AMOUNT ADDED



PERCENT DEVIATION FROM AMOUNT ADDED